Materials Science and Engineering C 33 (2013) 3160–3165

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

An electrochemical sensor based on 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole/carbon nanotube; detection of D-penicillamine in the presence of tryptophan

Ashraf Salmanipour [a,b], Mohammad Ali Taher [a], Hadi Beitollahi [c,*], Rahman Hosseinzadeh [d]

[a] Department of Chemistry, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran
[b] Young Researchers Society, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran
[c] Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran
[d] Department of Organic Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

ARTICLE INFO

Article history:
Received 25 August 2012
Received in revised form 12 March 2013
Accepted 23 March 2013
Available online 1 April 2013

Keywords:
D-penicillamine
Tryptophan
Modified glassy carbon electrode
Electrocatalysis
Carbon nanotubes

ABSTRACT

A glassy carbon electrode modified with 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT) and carbon nanotubes have been applied to the electrocatalytic oxidation of D-penicillamine (D-PA) which reduced the overpotential by about 470 mV with obviously increase the current response. Due to its strong electrocatalytic activity towards D-PA, the modified electrode can resolve the overlapped voltammetric waves of D-PA and tryptophan (TRP) into two well-defined voltammetric peaks with peak-to-peak separation in potentials of about 270 mV. This property allows to selective determination of D-PA in the presence of TRP. The transfer coefficient (a) for the electrocatalytic oxidation of D-PA and diffusion coefficient of this substance under the experimental conditions were also investigated. In phosphate buffer solution (PBS) of pH 8.0, the oxidation current increased linearly with two concentration intervals of D-PA, one is 1.0 to 10.0 μM and, the other is 10.0 to 800.0 μM. The detection limit (3σ) obtained by square wave voltammetry (SWV) was 0.1 μM. The proposed method was successfully applied to the determination of D-PA, and TRP in real samples.

1. Introduction

D-Penicillamine (D-PA) is an unphysiological sulfur-containing amino acid that belongs to the aminothiols family. This compound is derived from hydrolytic degradation of penicillin [1] but it does not have antibiotic activity. D-PA is a highly potent therapeutic agent used for many years in the treatment of various illnesses. It is the drug of first choice for patients with Wilson's disease [2], an autosomal recessive disorder of copper transport [2]. It is able to enhance the urinary excretion of others heavy metals such as lead, arsenic, mercury and zinc and therefore, is used as an oral chelating agent to treat conventional heavy metals intoxication [3]. It is also used as antifibrotic agent to treat scleroderma [4] and as antirheumatic drug to treat patients with active rheumatoid arthritis [5].

Several methods have been proposed for the determination of D-PA including high performance liquid chromatography with pre or post column derivatization [6], calorimetry [7], fluorometry [8], spectrophotometric [9], chemiluminescence [10], capillary electrophoresis [11] and NMR spectrometry [12]. One of the important limitations of LC techniques is the fact that this thiol lacks sufficient UV absorption so a pre or post-column derivatization procedure is normally required. Electrochemical methods are an alternative for the D-PA determination because they are cheap, simple, fast and sensitive [13–19].

Tryptophan (TRP) is an essential amino acid with diverse physiological roles, functioning both independently or via incorporation into the structure of larger molecules or polymers, such as proteins. It is a precursor for biologically important molecules, such as the neurotransmitter serotonin and the neurohormone melatonin [20]. Abnormal levels of serotonin and melatonin have been shown to be associated with depression [20] and Alzheimer's and Parkinson's diseases [20], respectively. It has been shown that the control of dietary intake of TRP (through food or supplements) and the resulting physiological concentrations in the human body has had a positive effect on the regulation of the synthesis of serotonin [21]. The regulation of the synthesis of serotonin leads to the controlled synthesis of melatonin [22] which promotes sleep. Electrochemical methods of detecting TRP [23–25] have shown promise compared to standard chromatographic [26,27] and electrophoretic [28] methods. However, electrochemical detection of TRP at unmodified electrode surfaces is not optimal owing to sluggish electron transfer processes [29], and in complex matrices is subject to interference from molecules with overlapping potentials.

The electrochemical methods using chemically modified electrodes (CMEs) have been widely used as sensitive and selective analytical methods for the detection of the trace amount of biologically important compounds [30–32]. One of the most important properties of CMEs have been their ability to catalyze the electrode process via

* Corresponding author. Tel.: +98 3426226613; fax: +98 3426226617.
E-mail address: h.beitollahi@yahoo.com (H. Beitollahi).

0928-4931/$ – see front matter
http://dx.doi.org/10.1016/j.msec.2013.03.041

significant decreasing of overpotential respect to relatively selective interaction of the electron mediator with the target analyte in a coordination fashion. These electrodes are capable to considerably enhance the selectivity in the electroanalytical methods [33–35].

Carbon nanotubes have attracted much attention during the past decade due to their unique mechanical, chemical and electrical properties [36]. Carbon nanotubes (CNT) with diameters in the range of 5–40 nm and up to several microns in length can now be produced in macro quantities [36]. According to their atomic structure, carbon nanotubes behave electrically as a metal or as a semiconductor [37]. They have many significant properties and can be used as attractive novel materials in electrochemical fields [38]. An important application of CNT is that they can be used as the electrode material in CNT paste electrodes [39–41] or CNT modified glassy carbon electrodes [42,43] to investigate the electrochemical properties of biomolecules.

The term niacin refers to both nicotinic acid and its amide derivative, nicotinamide (niacinamide). Both are used to form the coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP). Niacin is a member of the water soluble B-vitamin complex. The amino acid TRP can be converted to nicotinic acid in humans, therefore niacin is not really a vitamin provided that an adequate dietary supply of TRP is available. Nicotinic acid was isolated as early as 1867. In 1937 it was demonstrated that this substance cures the disease pellagra. The name niacin is derived from nicotinic acid + vitamin. The coenzymes NAD and NADP are required for many biological oxidation-reduction (redox) reactions. About 200 enzymes require NAD or NADP. NAD is mainly involved in reactions that generate energy in tissues by the biochemical degradation of carbohydrates, fats and proteins. NADP functions in reductive biosyntheses such as the synthesis of fatty acids and cholesterol. NAD is also required as a substrate for non-redox reactions. It is the source of adenosine diphosphate (ADP)-ribose, which is transferred to proteins by different enzymes. These enzymes and their products seem to be involved in DNA replication, DNA repair, cell differentiation and cellular signal transduction. Copper deficiency can inhibit the conversion of TRP to niacin. The drug PA has been demonstrated to inhibit the TRP-to-niacin pathway in humans; this may be due in part to the copper-chelating effect of PA [44]. Therefore, simultaneous determination of D-PA and TRP is important.

Thus, in this paper, we described initially the preparation and suitability of a 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT) modified glassy carbon nanotube electrode (BFTGCNE) as a new electrode in the electrocatalysis and determination of D-PA in an aqueous buffer solution. Then we evaluated the analytical performance of the modified electrode in quantification of D-PA in the presence of TRP.

2. Experimental

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 12, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the BFTGCNE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. D-PA, TRP and all other reagents were of analytical grade from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–11.0. Multiwalled carbon nanotubes (purity more than 95%) with o.d. between 10 and 20 nm, i.d. between 5 and 10 nm, and tube length from 0.5 to 200 μm were prepared from Nanostructured & Amorphous Materials, Inc.

2.2. Synthesis of 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT)

To a mixture of benzylazide (0.133 g, 1 mmol) and ethynylferrocene (0.210 g, 1 mmol), in 5 mL CH_2Cl_2/H_2O (1/1), sodium ascorbate (0.090 g, 45 mol%) and $CuSO_4.5H_2O$ (0.038 g, 15 mol%) were added under argon atmosphere and were stirred at an ambient temperature for 5 h. After addition of methylene chloride (15 mL) and H_2O (15 mL), the organic layer was separated, dried over Na_2SO_4, the solvent was removed under reduced pressure to obtain the crude product. The final product was purified by crystallization (methylene chloride:*n*-hexane) to obtain the pure product in 85% yield. M.p.: 158–160 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.09 (s, 5H), 4.32 (s, 2H), 4.73 (s, 2H), 5.56 (s, 2H), 7.28–7.31 (m, 2H), 7.36 (s, 1H), 7.38–7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 54.07, 66.73, 68.79, 69.73, 75.66, 118.75, 127.89, 128.69, 129.13, 134.93, 147.28.

2.3. Preparation of the modified electrodes

The preparation of modified GCE was performed by mechanically polishing a glassy carbon electrode with 0.05 μm Al_2O_3 in water slurry then, it was electrochemically activated in a 0.1 M sodium bicarbonate solution, and pouring 5 μL of CNT suspension (0.01 g/mL) onto the activated GCE surface. Finally for the preparation of BFT-CNT-GCE, CNT modified GCE was placed in a solution of 5% V/V ethanol and 0.1 M PBS (pH 6.0) containing 1.0 mM BFT. It was modified by 8 cycles of potential scan rate between 0.1 V and 0.55 V at 30 mVs^{-1}. In order to fabricate BFT modified GCE (BFT-GCE), the activated GCE was immersed in a solution of 5% V/V ethanol and 0.1 M PBS (pH 6.0) containing 1.0 mM BFT. The modification was performed with the same procedure that has been described for BFT-CNT-GCE.

3. Results and discussion

3.1. Electrochemical properties of BFTGCNE

To the best of our knowledge there is no prior report on the electrochemical properties and, in particular, the electrocatalytic activity of BFT in aqueous media. Therefore, we prepared BFTGCNE and studied its electrochemical properties in a 0.1 M PBS (pH 8.0) using CV (Fig. 1). Experimental results showed reproducible, well-defined, anodic and cathodic peaks with E_{pa}, E_{pc} and $E^{\circ\prime}$ of 330.0, 300.0 and 315.0 mV vs. Ag/AgCl/KCl (3.0 M) respectively.

The effect of the potential scan rate (ν) on electrochemical properties of the BFTGCNE was also studied by CV. Plots of the both anodic and cathodic peak currents (I_p) were linearly dependent on ν in the range of 30 to 1000 mV s^{-1} (Fig. 1A), indicating that the redox process of BFT at the modified electrode is diffusionless in nature [45].

The apparent charge transfer rate constant, k_s, and the charge transfer coefficient, α, of a surface-confined redox couple can be evaluated from CV experiments by using the variation of anodic and cathodic peak potentials with logarithm of scan rate, according to the procedure of Laviron [46]. Fig. 1B shows such plots, indicating that the E_p values are proportional to the logarithm of scan rate for scan rate values higher than 4.0 V s^{-1}. The slopes of the plots in Fig. 1B can be used to extract the kinetic parameters α_c and α_a (cathodic and anodic transfer coefficients, respectively). The slope of the linear segments are equal to –2.303RT/αnF and 2.303RT/(1 − α)nF for the cathodic and anodic peaks, respectively. The evaluated value for the α is 0.5.

Also, Eq. 1 can be used to determine the electron transfer rate constant between modifier (BFT) and electrode:

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nF\nu) - \alpha(1-\alpha)nF\Delta E_p/2.3RT \quad (1)$$

where $(1-\alpha)n_\alpha = 0.5$, ν is the sweep rate and all other symbols having their conventional meanings. The value of k_s was evaluated to be 12.7 s^{-1} using Eq. (1).